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(71)Applicant : SANYO ELECTRIC CO LTD

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(72)Inventor : TARUI HISAKI
YONEZU IKURO

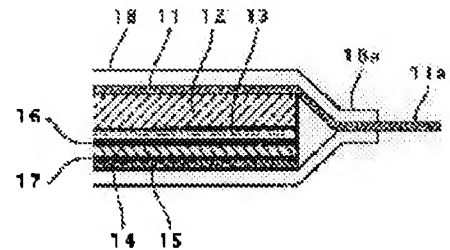
(54) LITHIUM BATTERY AND LITHIUM SECONDARY BATTERY

(57)Abstract:

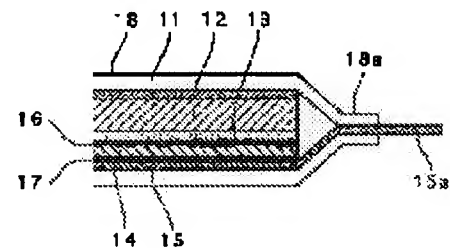
PROBLEM TO BE SOLVED: To provide a lithium battery and a lithium secondary battery each using silicon or an alloy mainly containing silicon for a negative electrode active material and an ion conductive solid electrolyte as an electrolyte, each having sufficient charge/discharge capacity and charge/discharge cycle property.

SOLUTION: Each of the lithium battery and the lithium secondary battery comprises a positive electrode, a negative electrode and the ion conductive solid electrolyte. Silicon or the alloy mainly containing silicon is used for the negative electrode active materials 2, 14 and a first mixture layer 16 is formed of the active material containing a component contained in the solid electrolyte, on an interface where the negative electrode active material and the solid electrolyte contact each other.

(A)



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]Use the alloy which this invention requires for the lithium cell and lithium secondary battery which have an anode, a negative electrode, and a solid electrolyte of ion conductivity, and makes silicon or silicon the active material of a negative electrode with a subject especially, and. It is related with a lithium cell and a lithium secondary battery using the solid electrolyte of ion conductivity as an electrolyte.

[0002]

[Description of the Prior Art]In recent years, the lithium cell and lithium secondary battery using oxidation of lithium and reduction of higher electromotive force came to be used as one of high power and the new style cells of high energy density.

[0003]Here, in such a lithium cell and a lithium secondary battery, battery characteristics, such as charge and discharge voltage, a charge-discharge cycle characteristic, and a conservation characteristic, are greatly influenced by the kind of active material used for an anode or a negative electrode.

[0004]And when the lithium metal was used for the active material of the negative electrode, the cell which has per weight and an energy density with per [high] volume could be obtained, but when charge and discharge were repeated and were performed, in the negative electrode, lithium deposited in the shape of a dendrite, and there was a problem of causing an internal short circuit.

[0005]For this reason, the aluminum electrochemically alloyed with lithium to a negative electrode in the case of charge, It is reported by the lithium secondary battery using silicon, tin, etc., and [Solid Statelronics, 113-115, p57 (1998)], In JP,10-255768,A etc., the lithium secondary battery which used silicon for the active material of the negative electrode is proposed noting that especially silicon has large theoretical capacity and a lithium secondary battery with high cell capacity is obtained.

[0006]However, in the case of the lithium secondary battery using lithium, the silicon to alloy, etc., in connection with charge and discharge, the active material of the negative electrode expanded and contracted greatly to the active material of the negative electrode, in connection with this volume change, the active material of the negative electrode carried out pulverization, the collecting characteristic worsened, and there was a problem that sufficient cycle characteristic was not acquired.

[0007]Although the nonaqueous electrolyte in which the solute which generally becomes an organic solvent from lithium salt was dissolved as an electrolyte in the conventional lithium cell is used, Generally such nonaqueous electrolyte is an inflammability, and had a problem in respect of safety, and there was a problem of this nonaqueous electrolyte spilling liquid, or the solvent of nonaqueous electrolyte reacting to an anode or a negative electrode, and the characteristic of a cell falling.

[0008]For this reason, in recent years, using the solid electrolyte of ion conductivity is examined as an electrolyte.

[0009]However, in the case of the lithium cell using the solid electrolyte of ion conductivity, contact with an electrode and a solid electrolyte is not enough, and ion conductivity worsens, When there is a problem that sufficient charge-and-discharge capacity is not obtained and lithium, the silicon to alloy, etc. are used for the active material of a negative electrode still as mentioned above, by the volume change of the active material of the negative electrode accompanying charge and discharge. Contact nature with a solid electrolyte fell further, and there was a problem that a charge-discharge cycle characteristic also worsened.

[0010]

[Problem(s) to be Solved by the Invention]This invention uses for the active material of a negative electrode the alloy which makes silicon or silicon a subject, and. It is what makes it a technical problem to solve the above problems in a lithium cell and a lithium secondary battery using the solid electrolyte of ion conductivity as an electrolyte, Improve the contact nature of the active material of a negative electrode and solid electrolyte using the alloy which makes silicon or silicon a subject, and sufficient charge-and-discharge capacity is obtained, and. When charge and discharge are repeated, let it be a technical problem to prevent contact nature with a solid electrolyte from falling, and to obtain sufficient charge-discharge cycle characteristic by the volume change of the active material of a negative electrode.

[0011]

[Means for Solving the Problem]In a lithium cell and a lithium secondary battery which have an anode, a negative electrode, and a solid electrolyte of ion conductivity in this invention in order to solve the above technical problems, The 1st mixed layer that an ingredient contained in the above-mentioned active material at a solid electrolyte contained in an interface to which an active material and a solid electrolyte of this negative electrode contact an active material of a negative electrode using an alloy which makes silicon or silicon a subject was formed.

[0012]And if the 1st mixed layer that an ingredient contained in an active material of a negative electrode at a solid electrolyte contained in an interface which an active material and a solid electrolyte of a negative electrode contact in this way is formed, The adhesion of an active material of a negative electrode and a solid electrolyte increases, ion conductivity improves, and sufficient charge-and-discharge capacity comes to be obtained, and. When charge and discharge are repeated, it is also controlled by volume change of an active material of a negative electrode that contact nature with a solid electrolyte falls, and sufficient charge-discharge cycle characteristic comes to be obtained by it.

[0013]It is preferred to use amorphous silicon and microcrystal silicon for it in this invention by the difference in a crystal structure, here, although amorphous silicon, microcrystal silicon, polycrystalline silicon, and single crystal silicon exist in silicon used for an active material of a negative electrode.

[0014]While a peak near [on Raman spectroscopic analysis and corresponding to an amorphous field in amorphous silicon] the 480-cm^{-1} is detected, a peak near [corresponding to a crystalline region] the 520-cm^{-1} is not detected substantially. A peak near [on Raman spectroscopic analysis and corresponding to a crystalline region in microcrystal silicon] the 520-cm^{-1} , Both peaks near [corresponding to an amorphous field] the 480-cm^{-1} are detected substantially, and microcrystal silicon comprises a crystalline region and an amorphous field substantially. On the other hand, while a peak near [on Raman spectroscopic analysis and corresponding to a crystalline region in polycrystalline silicon and single crystal silicon] the 520-cm^{-1} is detected, a peak near [corresponding to an amorphous field] the 480-cm^{-1} is not detected substantially.

[0015]And in an interface which an active material and a solid electrolyte of a negative electrode will contact if amorphous silicon and microcrystal silicon are used for an active material of a negative electrode as mentioned above, An ingredient contained in a solid electrolyte spreads and dissolves in the above-mentioned active material, and the 1st mixed layer that has a concentration gradient in which concentration of an ingredient of a solid electrolyte decreases toward the negative-electrode side comes to be formed.

[0016]If the 1st above mixed layer is formed in an interface which an active material and a solid electrolyte of a negative electrode contact here, The adhesion of an active material of a negative electrode and a solid electrolyte increases further, and ion conductivity improves further, and higher charge-and-discharge capacity comes to be obtained, and. When charge and discharge are repeated, a charge-discharge cycle characteristic where it was also further controlled by volume change of an active material of a negative electrode that contact nature with a solid electrolyte falls and which was further excellent in it by it comes to be obtained. Like [when an ingredient contained in a solid electrolyte will be dissolved in the above-mentioned active material in the 1st mixed layer as mentioned above / in a case of forming an intermetallic compound], An ingredient and an active material which are contained in a solid electrolyte by charge and discharge are not separated, adhesion does not necessarily fall, and a further outstanding charge-discharge cycle characteristic comes to be obtained. However, the 1st mixed layer can also be separately provided, as it is not limited to the following but an ingredient contained in a solid electrolyte is made to contain in the above-mentioned active material.

[0017]Since it becomes impossible to fully improve the adhesion of an active material of a negative electrode, and a solid electrolyte in providing the 1st mixed layer in an interface which an active material and a solid electrolyte of a negative electrode contact in this way when the thickness is thin, it is preferred that thickness of the 1st mixed layer shall be 0.1 micrometers or more.

[0018]As an alloy which makes a subject silicon used for an active material of a negative electrode, In silicon, IIIa fellows of the periodic table, IVa fellows, Va fellows, VIa fellows, Can use a thing which at least one sort of elements of VIIa fellows, a group VIII, Ib fellows (except for Cu), and IIb fellows made dope, and specifically, Scandium (Sc), titanium (Ti), and vanadium (V), chromium (Cr), Manganese (Mn), iron (Fe), cobalt (Co), nickel (nickel), Zinc (Zn), yttrium (Y), a zirconium (Zr), niobium (Nb), Molybdenum (Mo), technetium (Tc), a ruthenium (Ru), Rhodium (Rh), palladium (Pd), silver (Ag), cadmium (Cd), hafnium (Hf), tantalum (Ta), tungsten (W), a rhenium (Re), osmium (Os),

iridium (Ir), platinum (Pt), gold (Au), Mercury (Hg) and a lanthanoid series element which consists of gadolinium (Gd), a terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), a thulium (Tm), and ytterbium (Yb) lutetium (Lu) can be used. Since especially iron, cobalt and nickel which are the elements of a group VIII, Ib fellows, and IIb fellows, zinc, a ruthenium, rhodium, palladium, silver, cadmium, osmium, iridium, platinum, gold, and mercury have the high diffusion coefficient to inside of silicon, It is preferred to make these elements dope and it is made to make cobalt, zinc, iron, a zirconium, nickel, silver, an element chosen from manganese, and an element chosen from cobalt, zinc, iron, a zirconium, and nickel still more preferably dope more preferably. As for such an element, it is preferred to exist in the state where it dissolved in silicon.

[0019]And if the above elements are made to contain in silicon, it will be controlled that silicon carries out expansion contraction with a charge-and-discharge reaction, When charge and discharge are repeated, a charge-discharge cycle characteristic which it was further controlled by volume change of an active material of a negative electrode that contact nature with a solid electrolyte falls, and was further excellent by it comes to be obtained.

[0020]If the quantity increases too much in making the above elements contain in silicon, Since an effect which controls that silicon carries out expansion contraction with a charge-and-discharge reaction will no longer be acquired fully if there is little the quantity while quantity of silicon in an active material decreases and charge-and-discharge capacity falls, It is preferred to make quantity of the above-mentioned element in an active material into 0.1 to 30% of the weight of a range, and it is made to become 1 to 20% of the weight of a range more preferably.

[0021]If this interface is uneven shape in providing the 1st above mixed layer in an interface which an active material and a solid electrolyte of a negative electrode contact, Stress by expansion contraction of an active material accompanying a charge-and-discharge reaction is eased, and an active material and a solid electrolyte of a negative electrode are stabilized, it comes to contact, and a further outstanding charge-discharge cycle characteristic comes to be obtained.

[0022]Since the above effects will not fully be acquired if unevenness in the above-mentioned interface which an active material and a solid electrolyte of a negative electrode contact is small here, it is 1 micrometers or more that arithmetic-mean-roughness Ra in an interface is 0.1 micrometers or more desirable still more preferably. Arithmetic-mean-roughness Ra is provided in Japanese Industrial Standard (JIS B 0601-1994). In order to ease appropriately stress by expansion contraction of an active material accompanying a charge-and-discharge reaction, it is preferred that thickness of an active material is larger than above-mentioned arithmetic-mean-roughness Ra.

[0023]Although it is not limited in particular for a solid electrolyte used in this invention but a solid electrolyte currently generally used can be used, It is preferred to use a lithium ion conductivity inorganic solid electrolyte containing silicon so that adhesion with an active material of a negative electrode may improve via the 1st above-mentioned mixed layer.

[0024]And as a lithium ion conductivity inorganic solid electrolyte containing silicon, an inorganic solid electrolyte which consists of a sulfide or an oxide can be used.

[0025]As an inorganic solid electrolyte which consists of a sulfide containing silicon here, For example, $\text{Li}_2\text{S-SiS}_2$ or this $\text{Li}_2\text{S-SiS}_2$, Sulfide glass which consists of a compound with $\text{Li}_2\text{S-B}_2\text{S}_3$,

$\text{Li}_2\text{S-GeS}_2$, or $\text{Li}_2\text{S-P}_2\text{S}_5$, Furthermore, what added LiI , LiCl , LiF , LiBr , Li_3PO_4 , Li_2O , $\text{Li}_3\text{BO}_3\text{I}$, Li_2SO_4 , and Li_2CO_3 can be used for this sulfide glass.

[0026]As an inorganic solid electrolyte which consists of an oxide containing silicon, For example, $\text{Li}_2\text{O-SiO}_2$ or this $\text{Li}_2\text{O-SiO}_2$, Oxide glass which consists of a compound with $\text{Li}_2\text{O-B}_2\text{O}_3$, $\text{Li}_2\text{O-GeO}_2$, or $\text{Li}_2\text{O-P}_2\text{O}_5$, Furthermore, to this oxide glass. What added LiI , LiCl , LiF , LiBr , Li_3PO_4 , Li_2O , $\text{Li}_3\text{BO}_3\text{I}$, Li_2SO_4 , Li_2CO_3 , and Li_3N can be used.

[0027]In this invention, as the above-mentioned negative electrode, When the aforementioned active material can use what was formed filmy on a charge collector and is such a negative electrode, it is preferred to form the 2nd mixed layer that an ingredient contained in a charge collector at the above-mentioned active material contained also in an interface which an active material and a charge collector of a negative electrode contact.

[0028]And if the 2nd mixed layer that an ingredient contained in an active material of a negative electrode at a charge collector contained in an interface which an active material and a charge collector of a negative electrode contact in this way is formed, The adhesion of an active material of a negative electrode and a charge collector also increases, ion conductivity improves, and sufficient charge-and-discharge capacity comes to be obtained, and. When charge and discharge are repeated, it is also controlled by volume change of an active material of a negative electrode that contact nature with a charge collector falls, and sufficient charge-discharge cycle characteristic comes to be obtained by it.

[0029]It is preferred to use here what comprised material diffused in an active material of a negative electrode as the above-mentioned charge collector, for example, it is preferred to use what comprised at least one sort of materials chosen from copper, nickel, stainless steel, molybdenum, and tungsten.

[0030]In this invention, as an active material used for an anode, A transition metal oxide etc. which can carry out occlusion and discharge of the lithium currently generally used conventionally can be used, For example, LiCoO_2 , LiNiO_2 , and LiMn_2O_4 , Lithium containing transition metal oxides, such as LiMnO_2 and $\text{LiCo}_{0.5}\text{nickel}_{0.5}\text{O}_2$ and $\text{LiNi}_{0.7}\text{Co}_{0.2}\text{Mn}_{0.1}\text{O}_2$, and a metallic oxide which does not contain lithium, such as MnO_2 , can be used.

[0031]

[Example]Hereafter, give an example and the lithium secondary battery of this invention is explained concretely, and in the case of the lithium secondary battery in this example, a comparative example is given and it is shown clearly that a charge-discharge cycle characteristic improves. The lithium cell and lithium secondary battery in this invention are not limited to what was shown in the following example, but in the range which does not change that gist, are changed suitably and can be carried out.

[0032](Example 1) In this example, thickness used the electrolytic copper foil with which 18 micrometers and surface arithmetic-mean-roughness R_a were set to about 2 micrometers as a negative pole collector in a negative electrode. About surface arithmetic-mean-roughness R_a , using the sensing pin type surface type-like measuring instrument (Japanese vacuum-technology company make: Dektak ST), measurement distance was set as 2.0 mm and measured.

[0033]And the thin film of the negative electrode active material which consists of amorphous silicon from which thickness was set to about 4 micrometers by sputtering process was formed on the negative pole collector which consists of the above-mentioned electrolytic copper foil.

[0034]In forming here the thin film of the negative electrode active material which consists of amorphous silicon on the negative pole collector which consists of electrolytic copper foil, After adjusting the pressure in a reaction chamber to 0.01 Pa or less, introduced argon gas by flow 20sccm as sputtering gas, and the above-mentioned negative pole collector was heated at 100 **, and it adjusted so that the pressure in a reaction chamber might be set to 0.05 Pa. And negative bias is impressed to the above-mentioned negative pole collector from a DC high voltage power source, After cleaning the surface of a negative pole collector by reverse sputtering, a single crystal silicon wafer is used for a target, 2-kW electric power was made to act from a DC high voltage power source, the high voltage electric field was excited, sputtering of the single crystal silicon wafer of a target was carried out by the plasma by the glow discharge, and the thin film of the negative electrode active material which consists of amorphous silicon was formed on the above-mentioned negative pole collector.

[0035]And after forming the thin film of the negative electrode active material which consists of amorphous silicon on the negative pole collector which consists of electrolytic copper foil in this way, observe the interface with a transmission electron microscope, and. The place which investigated the concentration distribution of the composing element according to secondary ion mass spectrometry (SIMS), In [Cu in a negative pole collector spreads and dissolves in the amorphous silicon of negative electrode active material, and the 2nd mixed layer from which thickness was set to about 0.8 micrometer exists, and] this 2nd mixed layer, The concentration of Cu had a concentration gradient which decreases toward the thin film side of the negative electrode active material which consists of amorphous silicon.

[0036]Next, the thin film of the solid electrolyte whose thickness which LiPO_4 contained in $\text{Li}_2\text{S-SiS}_2$ by sputtering process is 0.8 micrometer was formed on the thin film of the negative electrode active material which consists of amorphous silicon formed on the negative pole collector as mentioned above.

[0037]In forming the thin film of the above-mentioned solid electrolyte here on the thin film of the negative electrode active material which consists of the above-mentioned amorphous silicon, After adjusting the pressure in a reaction chamber to 0.01 Pa or less, introduced argon gas by flow 20sccm as sputtering gas, and the above-mentioned negative pole collector was heated at 100 **, and it adjusted so that the pressure in a reaction chamber might be set to 0.05 Pa. And Li_2S , SiS_2 , LiPO_4 , and LiCoO_2 use for a target the sintered compact which became a weight ratio of 57:37:6, The high-frequency power of 300W was made to act from an RF generator, the electric field was excited, sputtering was carried out by the plasma by the glow discharge, and the thin film of the solid electrolyte which LiPO_4 contained was formed into $\text{Li}_2\text{S-SiS}_2$ on the thin film of the above-mentioned negative electrode active material.

[0038]And after forming the thin film of a solid electrolyte on the thin film of the negative electrode active material which consists of amorphous silicon in this way, observe the interface with a transmission electron microscope, and. The place which investigated the concentration distribution of

the composing element according to secondary ion mass spectrometry (SIMS), It had a concentration gradient in which the concentration of S which S contained in a solid electrolyte spreads and dissolves in the amorphous silicon of negative electrode active material, and the 1st mixed layer from which thickness was set to about 0.2 micrometer exists, and is contained in a solid electrolyte in this 1st mixed layer decreases toward the negative-electrode side.

[0039]Subsequently, the thin film of the negative electrode active material which consists of amorphous silicon on the negative pole collector which consists of electrolytic copper foil as mentioned above, It pierces and that by which the thin film of the solid electrolyte which LiPO_4 contained was formed one by one into $\text{Li}_2\text{S-SiS}_2$ was used so that it might be set to 17 mm in diameter.

[0040]On the other hand in an anode, Li_2CO_3 and CoCO_3 , Weighing was carried out and it mixed with the mortar so that the atomic ratio of Li:Co might be set to 1:1, and after pressing and carrying out pressing of this with a metallic mold 17 mm in diameter, in the air, it calcinated at 800 ** for 24 hours, and the baking body of LiCoO_2 was obtained. And the mortar ground the baking body of this LiCoO_2 and the LiCoO_2 powder in which mean particle diameter was set to 20 micrometers was obtained.

[0041]Acetylene black as 80 weight sections and a conducting agent for the above-mentioned LiCoO_2 powder And ten weight sections, The polytetrafluoroethylene as a binder was mixed at a rate of ten weight sections, pressing was pressed and carried out with a metallic mold 17 mm in diameter, and the positive electrode layer which became a pellet type was produced on the positive pole collector which consists of aluminium foil.

[0042]Subsequently, in the positive electrode layer which became a pellet type in this way, it is made to be the same as that of the case where the thin film of a solid electrolyte is formed in the field of a positive pole collector and an opposite hand on the thin film of the above-mentioned negative electrode active material, The thin film of the solid electrolyte whose thickness which LiPO_4 contained in $\text{Li}_2\text{S-SiS}_2$ by sputtering process is 0.5 micrometer was formed.

[0043]As a polymer electrolyte, polyethylene oxide is extended in thickness of 30 micrometers or less, and what clipped this in diameter of 17 mm was used.

[0044]And the thing which made the thin film 2 of the negative electrode active material which consists of amorphous silicon on the negative pole collector 1 as mentioned above, and the thin film 3 of the solid electrolyte which LiPO_4 contained in $\text{Li}_2\text{S-SiS}_2$ laminate as shown in drawing 1, Where the above-mentioned polymer electrolyte 7 is inserted between the things which made the positive electrode layer 5 and the thin film 6 of the solid electrolyte laminate on the positive pole collector 4, These are made to accommodate in the cell case 8 formed with the positive electrode can 8a and the negative electrode can 8b, While connecting the positive pole collector 4 to the positive electrode can 8a, the negative pole collector 1 was connected to the negative electrode can 8b, this positive electrode can 8a and negative electrode can 8b were electrically insulated with the insulating packing 9, and the lithium secondary battery which became a coin type was obtained.

[0045](Example 2) In forming the thin film of negative electrode active material in this example on the

negative pole collector which consists of electrolytic copper foil in the above-mentioned Example 1, with plasma CVD method. Thickness formed the thin film of the negative electrode active material which consists of microcrystal silicon set to about 4 micrometers, and the lithium secondary battery which became a coin type was obtained like the case of the above-mentioned Example 1 except it. [0046]In forming here the thin film of the negative electrode active material which consists of microcrystal silicon on the negative pole collector which consists of electrolytic copper foil, After adjusting the pressure in a reaction chamber to 0.01 Pa or less, introduced hydrogen (H_2) gas by flow 100sccm, the high frequency electric field was made to act by an RF generator, and the surface of the above-mentioned negative pole collector was cleaned by the plasma by this. Then, introduce the Silang (SiH_4) gas of material gas by flow 10sccm, and. Introduce the hydrogen (H_2) gas of carrier gas by flow 200sccm, and heat the above-mentioned negative pole collector at 120 **, and. Adjusted so that the pressure in a reaction chamber might be set to 10 Pa, and the high-frequency power of 550W was made to act from an RF generator, the plasma by the glow discharge decomposed the above-mentioned material gas, and the thin film of the negative electrode active material which consists of microcrystal silicon was formed on the above-mentioned negative pole collector.

[0047]After forming the thin film of the negative electrode active material which consists of microcrystal silicon on the negative pole collector which does in this way and consists of electrolytic copper foil, observe the interface with a transmission electron microscope, and. The place which investigated the concentration distribution of the composing element according to secondary ion mass spectrometry (SIMS), In [Cu in a negative pole collector spreads and dissolves in the microcrystal silicon of negative electrode active material, and the 2nd mixed layer from which thickness was set to about 0.8 micrometer exists, and] this 2nd mixed layer, The concentration of Cu had a concentration gradient which decreases toward the thin film side of the negative electrode active material which consists of microcrystal silicon.

[0048]When the thin film of a solid electrolyte is formed like the case of the above-mentioned Example 1 on the thin film of the negative electrode active material which consists of this microcrystal silicon, observe that interface with a transmission electron microscope, and. The place which investigated the concentration distribution of the composing element according to secondary ion mass spectrometry (SIMS), It had a concentration gradient in which the concentration of S which S contained in a solid electrolyte spreads and dissolves in the microcrystal silicon of negative electrode active material, and the 1st mixed layer from which thickness was set to about 0.2 micrometer exists, and is contained in a solid electrolyte in this 1st mixed layer decreases toward the negative-electrode side.

[0049](Comparative example 1) In this comparative example, the tantalum foil with which it was made to roll and 18 micrometers and surface arithmetic-mean-roughness Ra became 0.1 micrometer in thickness is used as a negative pole collector, It is made to be the same as that of the case of the above-mentioned Example 1 on the surface of the negative pole collector which consists of this tantalum foil, Formed the thin film of the negative electrode active material which consists of amorphous silicon, it is made not to provide the thin film of a solid electrolyte on the thin film of the negative electrode active material which consists of this amorphous silicon, and the lithium secondary battery which became a coin type was obtained like the case of the above-mentioned Example 1

except it.

[0050]When the thin film of the negative electrode active material which consists of amorphous silicon is formed here on the negative pole collector which consists of tantalum foil in this way, observe the interface with a transmission electron microscope, and. When the concentration distribution of the composing element was investigated according to secondary ion mass spectrometry (SIMS), into the amorphous silicon of negative electrode active material, Ta in a negative pole collector was not spread and the 2nd mixed layer was not formed.

[0051]Next, in 25 °C temperature conditions each lithium secondary battery of Examples 1 and 2 produced as mentioned above, It charges until negative-electrode capacity serves as 2000 mAh/g with the current of 100microA, and in the lithium secondary battery of the comparative example 1, since negative-electrode capacity was not charged to 2000 mAh/g, it charges to 4.2V.

Then, it discharges until discharge final voltage is set to 2.75V with the current of 100microA, It carried out by having repeated the charge and discharge of ten cycles by making this into one cycle, the capacity maintenance rate (%) of the capacity Q10 of 10 cycle eye to the capacity Q1 of 1 cycle eye in each lithium secondary battery was searched for by the following formula, and the result was shown in the following table 1.

[0052]

Capacity maintenance rate (%) = (Q10/Q1) x100 [0053]

[Table 1]

	実施例 1	実施例 2	比較例 1
容量維持率 (%)	98	98	24

[0054]As a result, compared with the lithium secondary battery of the comparative example 1, the capacity maintenance rate of 10 cycle eye is remarkably large, and the charge-discharge cycle characteristic of each lithium secondary battery of the above-mentioned Examples 1 and 2 was improving remarkably.

[0055](Example 3) In this example, thickness uses the aluminium foil in which 30 micrometers and surface arithmetic-mean-roughness Ra were set to about 0.2 micrometer as a positive pole collector, While forming in the field (2.5 cm x 2.5 cm) on this aluminium foil the thin film of the positive active material which consists of LiCoO₂ which used the mask, and from which thickness was set to 30 micrometers by sputtering process, The positive electrode tab was attached to the field of aluminium foil in which the thin film of positive active material is not formed.

[0056]In forming here the thin film of the positive active material which consists of LiCoO₂ by sputtering process on aluminium foil, After exhausting until it makes aluminium foil hold to a substrate holder, it sets in a reaction chamber and the pressure in this reaction chamber is set to 0.01 Pa or less, Argon gas was introduced by flow 20sccm as sputtering gas, and aluminium foil was heated at 400 °C, and it adjusted so that the pressure in a reaction chamber might be set to 0.05 Pa. And negative bias is impressed to aluminium foil from a DC high voltage power source, After cleaning

aluminium foil by reverse sputtering, make 2-kW electric power act from a DC high voltage power source, and a high voltage electric field is excited, Sputtering of the LiCoO_2 sintered compact of a target is carried out by the plasma by the glow discharge, After making 30 micrometers of LiCoO_2 deposit on the above-mentioned aluminium foil, the temperature of this aluminium foil was raised to 600 **, heat treatment was performed for 2 hours, and the thin film of the positive active material which consists of LiCoO_2 was formed.

[0057]Next, to the same field (2.5 cm x 2.5 cm), on the thin film of the positive active material which consists of LiCoO_2 formed in this way, use a mask, and by sputtering process. The thin film of the solid electrolyte whose thickness which LiPO_4 contained is 2 micrometers was formed into $\text{Li}_2\text{S-SiS}_2$.

[0058]In forming the thin film of the above-mentioned solid electrolyte here on the thin film of the positive active material which consists of LiCoO_2 , After forming the thin film of positive active material on aluminium foil as mentioned above, After adjusting the pressure in a reaction chamber to 0.01 Pa or less, introduced argon gas by flow 20sccm as sputtering gas, and the above-mentioned aluminium foil was heated at 100 **, and it adjusted so that the pressure in a reaction chamber might be set to 0.05 Pa. And Li_2S , SiS_2 , LiPO_4 , and LiCoO_2 use for a target the sintered compact which became a weight ratio of 50:35:15, The high-frequency power of 300W was made to act from an RF generator, the electric field was excited, sputtering was carried out by the plasma by the glow discharge, and the thin film of the solid electrolyte which LiPO_4 contained was formed into $\text{Li}_2\text{S-SiS}_2$ on the thin film of the above-mentioned positive active material.

[0059]Subsequently, the mask was used for the field (2 cm x 2 cm) on the thin film of the solid electrolyte formed in this way, and the thin film of the negative electrode active material which consists of amorphous silicon in which thickness was set to about 2 micrometers by sputtering process was formed in it.

[0060]In forming here the thin film of the negative electrode active material which consists of amorphous silicon on the thin film of a solid electrolyte, After adjusting the pressure in a reaction chamber to 0.01 Pa or less, argon gas was introduced by flow 20sccm as sputtering gas, the aluminium foil in which the thin film of the solid electrolyte was formed as mentioned above was heated at 100 **, and it adjusted so that the pressure in a reaction chamber might be set to 0.05 Pa. And use a single crystal silicon wafer for a target, make 2-kW electric power act from a DC high voltage power source, and a high voltage electric field is excited, Sputtering of the single crystal silicon wafer of a target was carried out by the plasma by the glow discharge, and the thin film of the negative electrode active material which consists of amorphous silicon was formed on the thin film of the above-mentioned solid electrolyte.

[0061]After forming the thin film of the negative electrode active material which consists of amorphous silicon on the thin film of a solid electrolyte in this way, observe the interface with a transmission electron microscope, and. The place which investigated the concentration distribution of the composing element according to secondary ion mass spectrometry (SIMS), It had a concentration gradient in which the concentration of S which S contained in a solid electrolyte spreads and dissolves in the amorphous silicon of negative electrode active material, and the 1st mixed layer from

which thickness was set to about 0.2 micrometer exists, and is contained in a solid electrolyte in this 1st mixed layer decreases toward the negative-electrode side.

[0062]And after forming in the same field (2 cm x 2 cm) the negative pole collector for which a mask is used and which thickness becomes from the thin film of the copper set to 2 micrometers by sputtering process on the thin film of the negative electrode active material which consists of amorphous silicon formed in this way, the negative electrode tab was attached on this negative pole collector.

[0063]In forming here the negative pole collector which consists of a copper thin film on the thin film of negative electrode active material, After adjusting the pressure in a reaction chamber to 0.01 Pa or less, argon gas was introduced by flow 20sccm as sputtering gas, the aluminium foil in which the thin film of negative electrode active material was formed as mentioned above was heated at 100 **, and it adjusted so that the pressure in a reaction chamber might be set to 0.05 Pa. And 2-kW electric power was made to act from a DC high voltage power source, the high voltage electric field was excited, sputtering of the copper plate used for the target by the plasma by the glow discharge was carried out, and the negative pole collector which consists of a copper thin film was formed on the thin film of the above-mentioned negative electrode active material.

[0064]After forming the negative pole collector which consists of a copper thin film on the thin film of the negative electrode active material which consists of amorphous silicon in this way, observe the interface with a transmission electron microscope, and. The place which investigated the concentration distribution of the composing element according to secondary ion mass spectrometry (SIMS), Copper of the negative pole collector spread and dissolved in the amorphous silicon of negative electrode active material, the 2nd mixed layer from which thickness was set to about 1.2 micrometers existed, and it had a concentration gradient in which the concentration of copper of a negative pole collector decreases toward the negative-electrode side in this 2nd mixed layer.

[0065]Next, the thin film 12 of the positive active material which consists of LiCoO_2 on the positive pole collector 11 which consists of aluminium foil as mentioned above as shown in drawing 2 (A) and (B), The thin film 13 of the solid electrolyte which LiPO_4 contained in $\text{Li}_2\text{S-SiS}_2$, The negative pole collector 15 which consists of the thin film 14 of the negative electrode active material which consists of amorphous silicon, and a copper thin film is formed one by one, and the 1st mixed layer 16 is formed between the thin film 13 of the above-mentioned solid electrolyte, and the thin film 14 of negative electrode active material, and. It is under [inert gas atmosphere] setting that by which the 2nd mixed layer 17 was formed between the thin film 14 of negative electrode active material, and the negative pole collector 15, Both sides of an aluminium sheet are made to accommodate in the armor body 18 which consists of a lamination object covered with resin, As the negative electrode tab 15a which was able to attach the positive electrode tab 11a attached to the positive pole collector 1 and the negative pole collector 15 was taken out from the obturation part 18a of the armor body 18, respectively, the armor body 18 was obturated, and the card shape lithium secondary battery as shown in drawing 3 was produced.

[0066]And also about the lithium secondary battery of Example 3 which was carried out in this way and produced. The place which searched for the capacity maintenance rate (%) of 10 cycle eye like the case of each lithium secondary battery of the above-mentioned Examples 1 and 2, The capacity

maintenance rate had become 98%, compared with the lithium secondary battery of the comparative example 1, the capacity maintenance rate of 10 cycle eye is remarkably large, and the charge-discharge cycle characteristic was improving remarkably.

[0067]

[Effect of the Invention]In the lithium cell and lithium secondary battery which have an anode, a negative electrode, and a solid electrolyte of ion conductivity in this invention as explained in full detail above, Having formed the 1st mixed layer that the ingredient contained in the above-mentioned active material at a solid electrolyte contained in the interface to which the active material and solid electrolyte of this negative electrode contact the active material of a negative electrode using the alloy which makes silicon or silicon a subject A sake, The adhesion of the active material of a negative electrode and a solid electrolyte increases, ion conductivity improves, and sufficient charge-and-discharge capacity comes to be obtained, and. When charge and discharge are repeated, the charge-discharge cycle characteristic where it was also controlled by the volume change of the active material of a negative electrode that contact nature with a solid electrolyte falls and which was excellent in it by it came to be obtained.

[Translation done.]